

New insights into the use of microwave technology for the hydrothermal valorisation of biomass: Microwave-assisted liquefaction, decomposition and fractionation reactions

Nuevos avances en el uso de micro-ondas para la valorización hidrotermal de biomasa: Reacciones de licuefacción, descomposición y fraccionamiento asistidas por micro-ondas

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Abstract

Microwave heating represents a potentially faster and more efficient and selective technology for the hydrothermal treatment of biomass in comparison to conventional heating based technologies. Specifically, microwave heating allows not only achieving a better process control, but also lower temperatures to be used. Furthermore, as water is highly effective in microwave energy absorption, the combination of hydrothermal conditions together with microwave assisted heating offers an interesting new technology for the design and development of novel hydrothermal processes. Herein, this work summarises some recent advances achieved at the Green Chemistry Centre of Excellence, Chemistry Department, University of York (UK) (<https://www.york.ac.uk/chemistry/research/green/research/publications/>), regarding the use of microwave technology for the valorisation of biomass under hydrothermal conditions, including microwave-assisted hydrothermal liquefaction (MA-HTL), decomposition (MA-HTD) and fractionation (MA-F). These processes are very timely and the work conducted represents a step-change in biomass pre-processing technologies, helping the development of novel routes for biomass valorisation.

Resumen

El calentamiento asistido por micro-ondas se considera una tecnología más rápida, eficiente y selectiva en comparación con otras técnicas de calentamiento convencionales para el tratamiento hidrotermal de biomasa. Específicamente, esta tecnología permite tanto lograr un mejor control del proceso, como el uso de menores temperaturas. Además, como el agua utilizada como disolvente en estos procesos es muy eficiente absorbiendo la energía emitida por las micro-ondas, la combinación de condiciones hidrotermales junto con un calentamiento asistido por micro-ondas, resulta en una alternativa novedosa y muy interesante para el diseño y desarrollo de nuevos procesos hidrotermales. En este contexto, el presente artículo resume algunos de los avances más recientes desarrollados en el Green Chemistry Centre of Excellence, del Departamento de Química de la Universidad de York (Reino Unido), ([https://](https://www.york.ac.uk/chemistry/research/green/research/publications/)

www.york.ac.uk/chemistry/research/green/research/publications/) sobre el uso de la tecnología de calentamiento por micro-ondas para la valorización hidrotermal de biomasa, incluyendo procesos de licuefacción, descomposición y fraccionamiento. Estas reacciones son de gran interés en la industria química y representan una contribución sustancial en el desarrollo de nuevos procesos para el pre-tratamiento de la biomasa, contribuyendo sustancialmente al desarrollo de nuevas rutas para la valorización sostenible de biomasa y residuos.

1. Introduction

The on-going movement to move from the existing petroleum-based society towards a renewable and sustainable bio-economy has led researches to explore the use of alternative feedstocks and develop novel and environmentally friendly processes for the production of bio-fuels and chemicals. With this in mind, lignocellulosic biomass has attracted increasing attention as a potential carbon-neutral raw material, while hydrothermal processes have gained extensive attention for the transformation of biomass into bio-fuels, valuable bio-chemicals and bio-materials^[1]. In particular, over the past few years, extensive work has been conducted addressing fuel and chemicals production using hydrothermal processes conducted using liquid hot compressed water at subcritical conditions; i.e. moderate temperatures (150-400 °C) and medium-to-high pressures (5-250 bar)^[2]. This work provides useful information about the effects of operating conditions and catalyst performance on several valorisation routes conducted at hydrothermal conditions, such as hydrolysis, liquefaction, solvolysis, fractionation and decomposition reactions.

However, new insights must be gained into the development of more sustainable valorisation strategies and new reactor designs and configurations for the expansion and development of these hydrothermal routes. In particular, the importance of process design, control and energy efficiency in the early stage technology development is highlighted as critical to the economic and environmental viability of these processes. Given this, the use of microwave heating to conduct hydrothermal

technologies to replace conventional heating during the valorisation of biomass [3-11]. Specifically, microwave heating is based on the high frequency rotation of polar molecules, which produces a quicker and higher heating of the species with high polarity [3, 4, 6-10]. This is very important for hydrothermal reactions, as the water used as the solvent is highly effective in microwave energy absorption. As a result, the combination of hydrothermal conditions together with microwave assisted heating has proven to be a very useful technology to achieve a selective and controllable biomass valorisation. It must also be borne in mind that cellulose, hemicellulose and lignin have different polarities, which allows the preferential solubilisation/fractionation of these structural biomass components if the conditions (temperature, pressure, time, catalyst) are carefully and smartly selected. [12, 13]; thus helping to the development of several bio-refinery concepts around microwave-assisted reactions [12, 14, 15].

Given this background, this work summarises some recent insights gained at the Green Chemistry Centre of Excellence, Chemistry Department, University of York (UK) into the use of microwave-assisted hydrothermal reactions for biomass valorisation. This includes microwave-assisted hydrothermal liquefaction (MA-HTL) of pine and spruce biomass, microwave-assisted hydrothermal decomposition (MA-HTD) of glycerol and microwave-assisted fractionation (MA-F) of rapeseed meal [12, 14, 15]. These processes are very timely and the work conducted represents a step-change in biomass pre-processing technologies, helping the development of novel routes for biomass valorisation.

2. Experimental

2.1 Microwave-assisted hydrothermal reactors

Two different microwave units were used for the different hydrothermal processes described in this work [12, 14, 15]. A Milestone Synthwave microwave reactor was used to conduct the MA-HTL and MA-HTD reactions for the valorisation of pine/spruce biomass and glycerol, respectively, in the presence of a co-precipitated Ni-Co/Al-Mg catalyst, while a CEM Discover II microwave facility was used to conduct the MA-F of rapeseed meal. The Milestone Synth-Wave microwave consists of a 1L water-cooled high-grade stainless steel reactor completely PTFE coated, which allows running elevated temperature and pressure (up to 300 °C and 199 bar, respectively) reactions. A magnetron connected through a waveguide to the bottom of the pressure vessel generates the microwave radiation needed to heat up the reactants. The pressure vessel is made of special stainless steel and is closed with a clamping device. The internal temperature is monitored and controlled by means of a thermo-well protected NiCr temperature sensor placed inside the reactor. The total internal pressure achieved inside the reactor is monitored by a pressure sensor. Before the experiment the reactor was filled with the required amount of N₂ at room temperature to achieve the desired pressure at reaction conditions using an internal calibration. The CEM Discover II (www.cem.com) microwave facility has a circular design of the waveguide, which focuses the microwave energy towards the reaction vessel; thus creating a highly uniform field of microwave energy in the centre of the cavity where the reaction vessel rests. This configuration provides consistent heating and the ability to rapidly heat up to the temperature of the experiment.

| Pine/Spruce biomass | | Rapeseed meal | |
|---------------------------|------------|---------------------------|------------|
| Proximate analysis (wt.%) | | Proximate analysis (wt.%) | |
| Moisture | 6.78 ±0.58 | Moisture | 7.26 |
| Ash | 1.37±0.01 | Ash | 1.31 |
| Volatiles | 58.4±0.57 | Volatiles | 45.09 |
| Fixed carbon | 17.07±1.08 | Fixed carbon | 32.04 |
| Fibre analysis (wt.%) | | Fibre analysis (wt.%) | |
| Cellulose | 62.42 | Cellulose | 12.41±0.33 |
| Hemicellulose | 27.01 | Hemicellulose | 7.16±0.26 |
| Lignin | 9.20 | Lignin | 32.39±2.47 |
| Protein | 0 | Protein | 39.47±1.17 |
| Elemental analysis (wt.%) | | Elemental analysis (wt.%) | |
| C | 47.75±0.24 | C | 41.54±0.19 |
| H | 6.20±0.05 | H | 6.29±0.17 |
| N | 0 | N | 6.32±0.19 |
| O* | 46.05±0.35 | O* | 45.86±0.17 |
| HHV (MJ/kg) | 19.21±0.15 | HHV (MJ/kg) | 17.07±0.29 |

*Oxygen was calculated by difference

Table 1. Proximate, fibre and elemental analyses and calorific value of pine/spruce biomass and rapeseed meal.

Tabla 1. Análisis inmediato, elemental estructural y poder calorífico de la biomasa de pino/haya y de la harina de colza.

2.2 Feedstocks characterisation

Croda International (Widnes, UK) provided the rapeseed meal used for the microwave-assisted hydrothermal experiments. The biomass used for the microwave-assisted hydrothermal liquefaction work consists of a palletised mixture of pine and spruce wood. The most important physicochemical properties of these materials are listed in Table 1. Proximate analyses were performed according to standard methods (ISO-589-1981 for moisture, ISO-1171-1976 for ash and ISO-5623-1974 for volatiles). Glycerol was purchased from Sigma Aldrich. A 30 wt.% glycerol/water solution, representing a typical glycerol concentration in a biodiesel production by-product stream, was used for the MA-HTD experiments.

3. Results and discussion

3.1 Microwave-assisted hydrothermal liquefaction of pine/spruce biomass

Microwave-assisted hydrothermal liquefaction (MA-HTL) was used for the valorisation of a mixture of pine and spruce biomass, examining the effects of the temperature (150-250 °C), pressure (50-120 bar), time (0-2 h) and catalyst amount (Ni-Co/Al-Mg; 0-0.25 g catalyst/g biomass) [14]. The experimental results revealed that the combination of hydrothermal conditions coupled with microwave heating resulted into a very promising route for the production of a bio-oil with suitable physicochemical fuel properties. The operating conditions exerted a significant influence on the process; the overall biomass conversion and the yields to gas and bio-oil varied by 13-77%, 7-67% and 1-29%, respectively. The bio-oil produced

consisted of a complex mixture of esters (0-30%), aldehydes (4-69%), ketones (0-35%), alcohols (0-14%), phenols (0-83%), acids (0-28%), cyclic compounds (0-38%), acetates (0-11%), ethers (0-27%) and furans (0-12%). The proportions of C, H and O in the liquid shifted by 2-70 wt.%, 4-11 wt.% and 27-87 wt.%, which varied the Higher Heating Value (HHV) between 4 and 28 MJ/kg.

Optimum conditions were sought for the production of liquid biofuels and platform chemicals considering three different scenarios. The first and the second optimisations were directed towards the production of a liquid bio-fuel. In particular, the first was aimed at maximising the bio-oil yield and HHV, while the second also includes the minimisation of the relative amount of carboxylic acids in the bio-oil. The third comprises the production of a bio-oil containing a high amount of phenolic compounds to be used as a starting material to produce a wide spread range of chemicals as well as green and sustainable fuel additives to improve the oxidation stability of other liquid bio-fuels. Figure 1 summarises the results obtained during the optimisation of the process. The three optima were found at high temperature (250 °C) and long reaction time (112-116 min) employing a large amount of catalyst (0.17-0.25 g catalyst/g biomass). A good compromise between bio-oil yield (27%) and HHV (20 MJ/kg) (Opt. 1) took place at medium pressure (80 bar). Increasing the pressure up to 120 bar helps minimise the relative amount of carboxylic acids (Opt. 2) in the bio-oil (2%) maintaining a relatively high bio-oil yield (25%) and HHV (19 MJ/kg). The maximum production of phenolic compounds (Opt. 3) occurred at 98 bar.

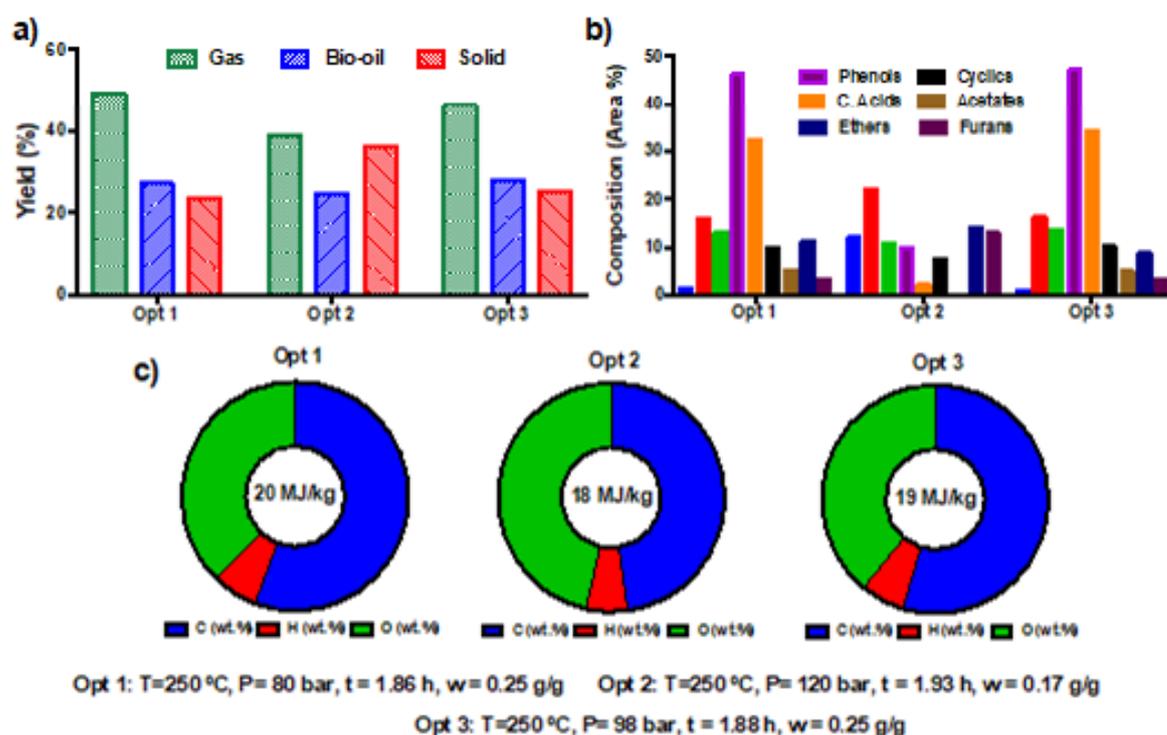


Figure 1. Optimum conditions: a) Product distribution, b) bio-oil chemical analysis and c) bio-oil elemental analysis and HHV.

Figura 1. Condiciones óptimas: a) Distribución de productos, b) análisis químico del bio-oil y c) análisis elemental y PCS del bio-oil.

In addition, an energetic assessment was conducted. At optimum conditions the total electric energy required for running the microwave reaction is 0.164 kWh (0.59 MJ), which corresponds to 59 MJ/kg of biomass. The theoretical total energy required to heat up the feedstock (biomass and water) is around 0.47 MJ, which gives a microwave energy efficiency of around 80%. The energy efficiency for bio-oil production was estimated as the output energy, including the calorific value of the bio-oil and the energy that can be recovered from water cooling (from 250 °C to 40 °C, 0.44 MJ), divided by the total microwave energy (input energy). Energy efficiencies between 82% (opt 2) and 84% (Op 1 and 3) were achieved at optimum conditions. Therefore, our results revealed that this microwave-assisted hydrothermal process allowed converting biomass into a high-energy, phenol-rich bio-oil at much lower temperatures (250 °C) than those commonly used during hydrothermal liquefaction (300-350 °C) [1, 2, 16-19]. Hence, this emerging technology represents a step-change in the future energy and chemical production, helping to the development of novel and more energy efficient routes for biomass valorisation.

3.2 Microwave-assisted hydrothermal decomposition of glycerol

Glycerol upgrading has recently been highlighted as a potentially critical aspect of the economic and environmental viability of future biodiesel-based bio-refineries. For the first time, we developed a microwave-assisted hydrothermal decomposition (MA-HTD) process for its transformation into value-added chemicals. We thoroughly examined the effects of the temperature (150-250 °C), pressure (50-120 bar), reaction time (0-2 h) and catalyst mass (5-15 wt.%; Ni-Co/Al-Mg) using of a 30 wt.% glycerol solution [15]. This process turned out to be a

very promising alternative for glycerol valorisation. In particular, the global glycerol conversion and the carbon converted to gas and liquid products varied by 5-54%, 0-21% and 3-42%, respectively. The parametric study conducted revealed that increasing the temperature, reaction time and/or catalyst amount increased glycerol decomposition due to the positive kinetic effects that these variables have on the process. Very interestingly, we also found that the pressure exerted two counteracting effects: a positive kinetic effect and a thermodynamic inhibitory influence; this latter being accounted for by the lower dielectric loss factor of water at high pressures. The liquid phase was made up of monohydric (10-62 wt.%) and polyhydric (0-46 wt.%) alcohols, carboxylic acids (0-9 wt.%) and C3-ketones (0-80 wt.%).

Our process was optimised for the selective production of different liquid products. The first scenario comprised the maximisation of the production of valuable liquids without considering their selectivity. For the other three optimisations, the liquid production was maximised, but also it was the selectivity towards some liquid products, including the production of C3-ketones, polyhydric and monohydric alcohols (Figure 2). The highest glycerol conversion along with the highest selectivity towards liquid products (X gly and CC liq) was achieved using an elevated temperature and a large catalyst amount for a long reaction time at relatively high pressure. This maximises the glycerol conversion and minimises the formation of gases. To maximise the proportion of C3-ketones (Opt. 2), it is necessary to use a medium temperature, low pressure and few catalyst mass for a long reaction time. Optimum conditions for the production of polyhydric alcohols (Opt. 3) were high temperature and catalyst/glycerol ratio together with a medium catalyst mass and a relatively long reaction time.

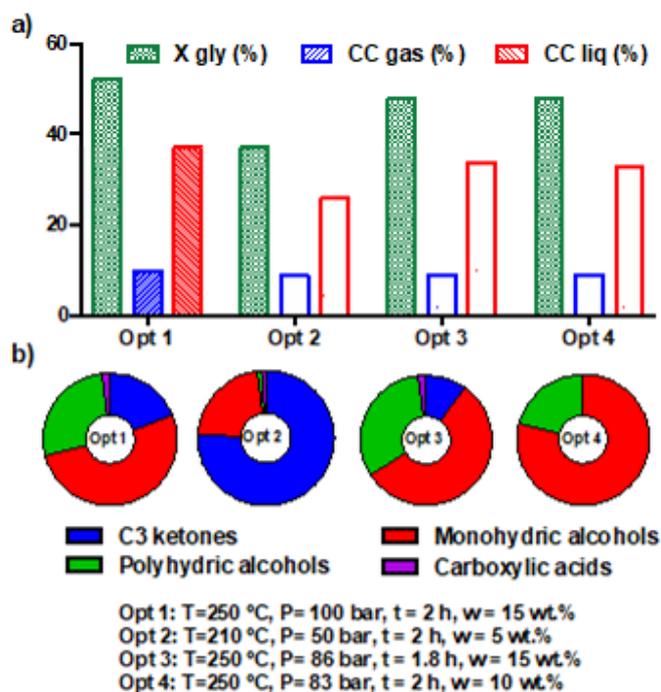


Figure 2. Optimum conditions: a) Product distribution: glycerol conversion, CC gas and CC liq and b) Liquid product distribution (wt. %).

Figura 2. Condiciones óptimas: a) Distribución de productos: conversión de glicerina, CC gas y CC liq y b) Distribución de productos del líquido.

The maximisation of monohydric alcohols implies the use of conditions for the temperature and pressure where the formation of liquid products is highly favoured combined with large catalyst amounts to favour the extension of the reactions in the liquid phase towards end products, along with a moderate reaction time to minimise their subsequent transformation into small oxygenated and gases. The highest proportion of monohydric alcohols in the liquid (Opt. 4) was achieved at high temperature, long reaction time and using medium both pressure and catalyst quantity. This implies a decrease in the catalyst amount together with a small increase in reaction time in comparison with optimum conditions for the production of polyhydric alcohols to shift the reaction towards the production of liquid end products without a further decomposition to gases. These results represent a step-change in the development of novel processes for the valorisation of glycerol as putting the effort into process control could pay off in terms of getting the maximum value from glycerol by-products and make a major contribution to rendering the entire biodiesel biorefinery more economically and environmentally viable.

3.2 Microwave-assisted hydrothermal fractionation

Microwave-assisted hydrothermal fractionation was used for the co-production of high-purity lignin and

cellu- and xylo- oligosaccharides from rapeseed meal using acetic acid as the catalyst. The effects of the temperature (150-210 °C), reaction time (0-60 min) and catalyst amount (1-4 mol/L, CH₃COOH) were thoroughly investigated on the process. Our results helped to the development of a new refinery concept around rapeseed meal, thus allowing the transformation of this material into value-added gas, solid, and liquid fractions [12]. The operating conditions significantly influenced the yield and properties of these fractions. In particular, the solid consisted of high purity lignin (26-88 wt.%) together with unreacted cellulose (0-28 wt.%), hemicellulose (0-28 wt.%) and proteins (11-28 wt.%). The relative amounts (wt.%) of C, H, O and N in the solid fraction shifted between 46-63, 5.8-6.4, 28-42 and 2-6, respectively. An increase in the temperature and/or reaction time led to an increase in the liquid yield at the expenses of the solid yield due to the solubilisation of the cellulosic and hemicellulosic contents of the feedstock into the liquid product. Very interestingly, it was found that acetic acid, a renewable-based catalyst that can also be produced from biomass, exerted a positive catalytic effect, promoting the solubilisation of cellulose and hemicellulose in the liquid fraction and more importantly, preventing the formation of humins. The liquid phase comprised oligo- and mono/di-saccharides (33-51 C-wt.%, 0-3 C-wt.% and 0-6 C-wt.%) and carboxylic acids (40-62 C-wt.%) dissolved in water.

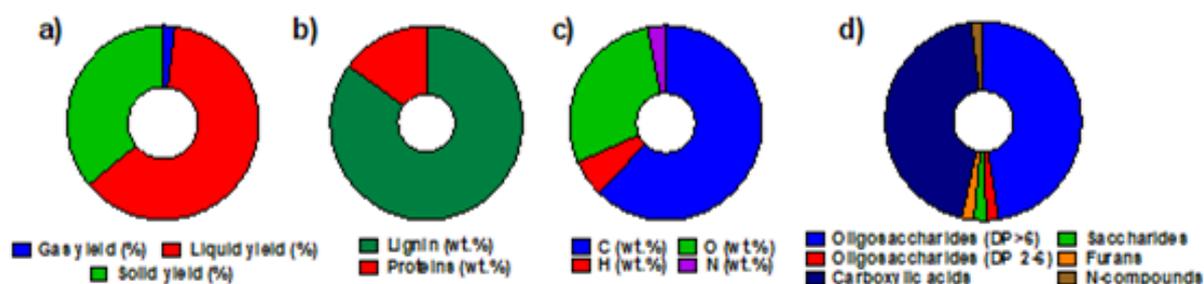


Figure 3. Optimum conditions: a) Product distribution, b) Solid composition, c) Solid elemental analysis and d) Liquid product composition.

Figura 3. Condiciones óptimas: a) Distribución de productos, b) Composición del sólido, c) Análisis elemental del sólido y d) Composición química del producto líquido.

This microwave fractionation process was optimised aiming to maximise the lignin content of the solid fraction produced and minimise of the proportions of cellulose, hemicellulose and proteins in this solid fraction. In addition, the temperature, time and acetic acid concentration were also minimised for energy-saving purposes. Optimum conditions were found at 186 °C using a concentration of acetic acid of 1 mol/L for a total reaction time of 2 min. These conditions allowed the selective conversion of 36% of the original feedstock into high purity (85 wt.%) lignin. The elemental analysis of the lignin produced (without taking the N content into account) was very similar to the results reported by other authors addressing lignin isolation from other types biomass [13, 20, 21]. This confirmed that all the lignin and the vast majority of the proteins initially presented in the

original rapeseed meal remained in the solid during the isolation process. The rest (63%) was transformed into a mixture of soluble oligosaccharides containing the acetic acid used in the experiment. To increase the effectiveness and sustainability of this process, acetic acid was recovered from the oligosaccharide solution. This allowed the simultaneous production of sugar-free, relatively high purity lignin (85 wt.%) along with a sugar rich solid fraction comprising oligo- and mono/di-saccharides (92 C-wt.%) with several applications in the chemical and biological industries.

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References

- [1] Gollakota ARK, Kishore N, Gu S. A review on hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews*. 2018;81:1378-92.
- [2] Dimitriadis A, Bezergianni S. Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review. *Renewable and Sustainable Energy Reviews*. 2017;68:113-25.
- [3] Budarin VL, Clark JH, Lanigan BA, Shuttleworth P, Macquarrie DJ. Microwave assisted decomposition of cellulose: A new thermochemical route for biomass exploitation. *Bioresource technology*. 2010;101:3776-9.
- [4] Budarin VL, Shuttleworth PS, Dodson JR, Hunt AJ, Lanigan B, Marriott R, et al. Use of green chemical technologies in an integrated biorefinery. *Energy Environ Sci*. 2011;4:471-9.
- [5] De bruyn M, Fan J, Budarin VL, Macquarrie DJ, Gomez LD, Simister R, et al. A new perspective in bio-refining: levoglucosenone and cleaner lignin from waste biorefinery hydrolysis lignin by selective conversion of residual saccharides. *Energy Environ Sci*. 2016;9:2571-4.
- [6] de Melo EM, Clark JH, Matharu AS. The Hy-MASS concept: hydrothermal microwave assisted selective scissoring of cellulose for in situ production of (meso) porous nanocellulose fibrils and crystals. *Green Chem*. 2017;19:3408-17.
- [7] Fan J, De bruyn M, Budarin VL, Gronnow MJ, Shuttleworth PS, Breeden S, et al. Direct microwave-assisted hydrothermal depolymerization of cellulose. *J Am Chem Soc*. 2013;135:11728-31.
- [8] Fan J, De bruyn M, Zhu Z, Budarin V, Gronnow M, Gomez LD, et al. Microwave-enhanced formation of glucose from cellulosic waste. *Chemical Engineering and Processing: Process Intensification*. 2013;71:37-42.
- [9] Li T, Remón J, Jiang Z, Budarin VL, Clark JH. Towards the development of a novel "bamboo-refinery" concept: Selective bamboo fractionation by means of a microwave-assisted, acid-catalysed, organosolv process. *Energy Conversion and Management*. 2018;155:147-60.
- [10] Li T, Remón J, Shuttleworth PS, Jiang Z, Fan J, Clark JH, et al. Controllable production of liquid and solid biofuels by doping-free, microwave-assisted, pressurised pyrolysis of hemicellulose. *Energy Conversion and Management*. 2017;144:104-13.
- [11] Matharu AS, de Melo E., Remón J., Wang S., Abdulina A, Kontturi E.. Processing of Citrus Nanostructured Cellulose: A Rigorous Design-of-Experiment Study of the Hydrothermal Microwave-Assisted Selective Scissoring Process. *ChemSusChem*. 2018;11:1344-53.
- [12] Remón J, Matharu AS, Clark JH. Simultaneous production of lignin and polysaccharide rich aqueous solutions by microwave-assisted hydrothermal treatment of rapeseed meal. *Energy Conversion and Management*. 2018;165:634-48.
- [13] Zhou L, Budarin V, Fan J, Sloan R, Macquarrie D. Efficient Method of Lignin Isolation Using Microwave-Assisted Acidolysis and Characterization of the Residual Lignin. *ACS Sustainable Chemistry & Engineering*. 2017;5:3768-74.
- [14] Remón J, Randall J, Budarin VL, Clark JH. Production of bio-fuels and chemicals by microwave-assisted, catalytic, hydrothermal liquefaction (MAC-HTL) of a mixture of pine and spruce biomass. *Green Chemistry*. 2019;21:284-99.
- [15] Remón J, Zhu G, Budarin VL, Clark JH. Analysis and optimisation of a microwave-assisted hydrothermal process for the production of value-added chemicals from glycerol. *Green Chemistry*. 2018;20:2624-36.
- [16] Elliott DC, Biller P, Ross AB, Schmidt AJ, Jones SB. Hydrothermal liquefaction of biomass: developments from batch to continuous process. *Bioresource technology*. 2015;178:147-56.
- [17] Kumar M, Olajire Oyedun A, Kumar A. A review on the current status of various hydrothermal technologies on biomass feedstock. *Renewable and Sustainable Energy Reviews*. 2018;81:1742-70.
- [18] Thiruvankadam S, Izhar S, Yoshida H, Danquah MK, Harun R. Process application of Subcritical Water Extraction (SWE) for algal bio-products and biofuels production. *Applied Energy*. 2015;154:815-28.
- [19] Toor SS, Rosendahl L, Rudolf A. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy*. 2011;36:2328-42.
- [20] Zhou L, Santomauro F, Fan J, Macquarrie D, Clark J, Chuck CJ, et al. Fast microwave-assisted acidolysis: a new biorefinery approach for the zero-waste utilisation of lignocellulosic biomass to produce high quality lignin and fermentable saccharides. *Faraday Discuss*. 2017;202:351-70.
- [21] Zhou S, Liu L, Wang B, Xu F, Sun R. Microwave-enhanced extraction of lignin from birch in formic acid: Structural characterization and antioxidant activity study. *Process Biochemistry*. 2012;47:1799-806.